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#### How to cite:

Zhang, X. F. and Qin, R. S. (2015). Segregation of copper in an Fe–Cu alloy under pulsed electric current. *Philosophical Magazine Letters*, 95(7) pp. 367–375.

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Version: Accepted Manuscript

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1080/09500839.2015.1069415>

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## Segregation of copper in an Fe-Cu alloy under pulsed electric current

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### Abstract

Effect of electric current on the segregation of copper precipitates in the Fe-13.6Cu alloy is evaluated. Results of this approach present two stages of segregation, namely, grain-boundary segregation during the solidification and interphase segregation during the decomposition of a solid solution. The segregation becomes apparent not only because the thermodynamic barrier for segregation is decreased, but also because the diffusion is greatly enhanced. Based on the thermodynamic and kinetic aspects, the segregation process under electric current would be of great interest and of physical importance because this kind of electric current-induced segregation was much stronger than the thermal diffusion segregation.

**Keywords:** segregation; electric current; electrical conductivity; free energy; diffusion

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## 1. Introduction

Segregation of a solute to surface or an internal interface of a solid produces of material with a discrete composition and its own set of properties that can have important (and often deleterious) effects on the overall properties of the material [1-4]. These zones with an increased concentration of solute can lead to interface fracture as a result of creep embrittlement, stress relief cracking, grain boundary corrosion, and some kinds of intergranular stress corrosion cracking [1-4]. Accordingly, the structural integrity of the material depends not only on the properties of the matrix, but also greatly on the properties of the interface in between. Basically, the segregation is closely related to the process of diffusion, in particular the thermal diffusion segregation is most concerned due to the enhanced diffusion at high temperatures [1-4]. In the application of pulsed electric current, the atomic diffusion can be enhanced [5,6] and the thermodynamic barrier for phase transformations can be decreased [7,8]. These suggest that segregation in materials would be greatly exacerbated when passing a pulsed electric current. Up to now, there has no report on the application of electric current to affect solute atoms segregation in alloys during metallurgy except for lead inclusions segregation in Cu-Zn alloys [9] as reported recently. The Fe-Cu system is distinguished by the limited mutual solubility of iron and copper and the extremely small solubility of copper in cementite (normally the microstructure of a medium carbon steel at room temperature is composed of  $\alpha$ -Fe and cementite) [10-12]. Therefore, the Fe-Cu alloy with extremely low mutual solubility of copper in iron and cementite makes this an attractive system for investigating basic segregation behaviour under pulsed electric current. Moreover, prediction and control of the failures resulted by segregation remains one of the most urgent and vexing challenges facing the materials engineer.

Here, pulsed electric current [13,14], as an instantaneous high energy input method, is applied to the copper precipitation during solidification and subsequent its precipitation from a supersaturated solid solution. Results of this approach are applied to the Fe-Cu system presenting two stages of segregation, namely, grain-boundary segregation during the solidification and interphase segregation during the decomposition of a solid solution. Based on the thermodynamic and kinetic aspects, a possible segregation process of copper precipitates in an Fe-Cu alloy under electric current will be given in this Letter, which would

be of great interest and of physical importance if this kind of electric current-induced segregation was much stronger than the thermal diffusion segregation.

## 2. Experimental procedures

An Fe-13.6Cu alloy with the chemical composition (wt.%) 0.63C, 0.23Si, 0.85Mn and 13.6Cu was used. According to the calculated phase diagram by Thermo-Calc software in Figure 1, at 1100 °C the maximum solubility of copper in austenite is approximately 6 wt.% while that of copper in ferrite is approximately 0.5 wt.% at 700 °C. The Fe-13.6Cu system containing a large amount of copper that exceeds the solubility limit in austenite was chosen to simultaneously study the effect of pulsed electric current on the copper precipitation during solidification (Stage I in Figure 1) and subsequent its precipitation from a supersaturated solid solution (Stage II in Figure 1). The alloy was placed in a graphite crucible and heated to be molten state at approximately 1520 °C for 5 min. Subsequently, the solidification started when the power of the furnace was switched off. Finally, the samples were furnace cooled to room temperature. In order to apply the electric current into the investigated alloy, a pair of steel bars was submerged into the liquid alloy to act as the electrodes. In order to determine the effect of electric current, two sets of experiments were carried out, one without electric current and the other with electric current. The experimental procedures were identical except for the application of electric current. The frequency of the applied pulsed electric current was 1 Hz and the duration of each pulse was 60  $\mu$ s. The density of the pulsed electric current was  $1.16 \times 10^6$  A/m<sup>2</sup>. In the whole processes of solidification and phase transformations, the pulsed electric current was applied ( $\sim 30$  min). The furnace-cooled samples were longitudinally sectioned and polished for metallographic examination. The configuration of the copper precipitates was preliminary examined by optical microscopy and scanning electron microscope using a microscope equipped for energy-dispersive spectroscopy (SEM-EDS). The overall distribution of the precipitates in the micron-size can be confirmed. The configuration of the precipitates before and after the electric current was further identified by transmission electron microscopy (TEM) to confirm their distribution in the nano-size. For the TEM observation, specimens were mechanically polished to a thickness of 30  $\mu$ m, punched to the disc specimens with 3 mm in diameter by a brass cutter. The thin film specimens were electropolished using a solution of 50 g anhydrous sodium chromate in 300 ml glacial acetic acid at room temperature and observed by TEM operated at an acceleration

voltage of 200 kV. The electrical conductivity of the investigated alloys with and without pulsed electric current was measured by a microhmmeter.

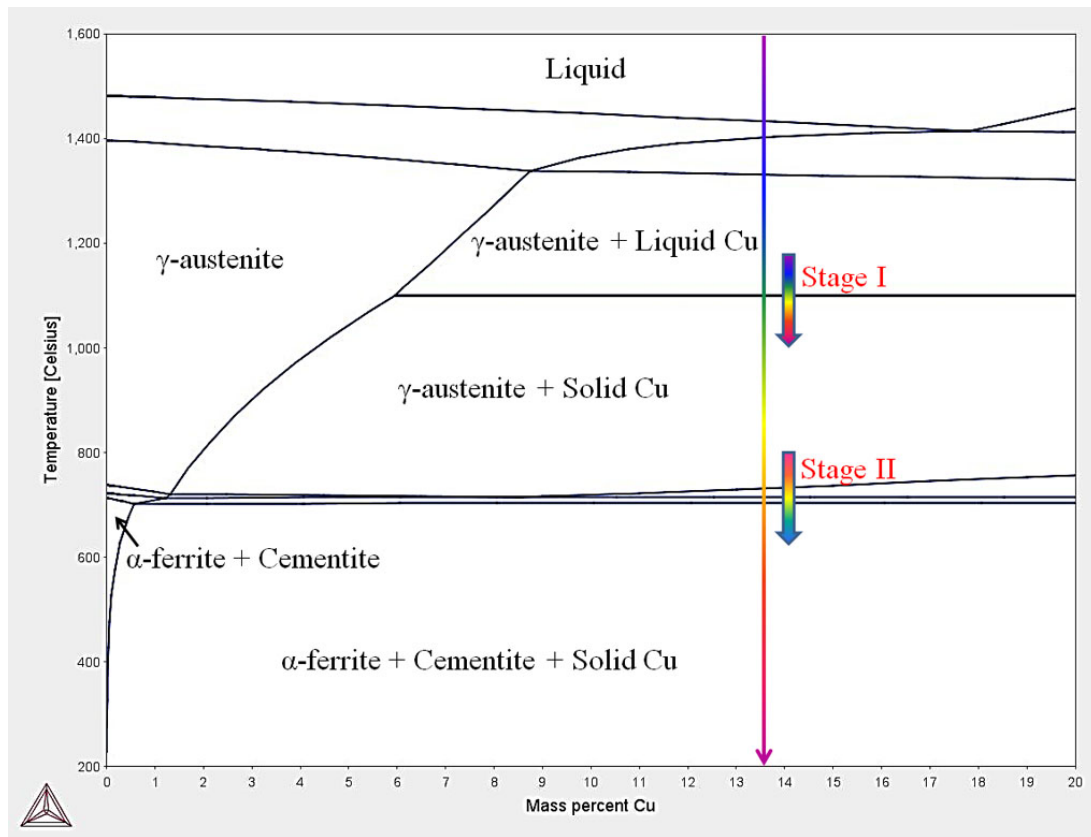


Figure 1. Phase diagram of Fe-Cu alloy calculated by Thermo-Calc software. Thin arrow indicates the cooling process of the investigated alloys while thick arrows represent the phase transformations. Stage I is for solidification of liquid copper and Stage II is for decomposition of austenite.

### 3. Results and discussion

The optical micrographs for the specimens before and after the electric current are presented in Figure 2, respectively. In the case of Figure 2a and b without the pulsed electric current, majority of copper precipitates ( $\sim 84.6\%$ ) were dispersed in the matrix with the average size of  $18 \mu\text{m}$  in diameter. Only one trigeminal grain boundary can be observed in Figure 2a, so the grain size of the matrix without electric current is also very large ( $>2 \text{ mm}$ ). Interestingly, after the application of the electric current the distribution of copper precipitates exhibits an apparent tendency, that is, all precipitates segregated to grain boundaries (Figure 2c and d). Many precipitates had been linked each other at the grain boundaries, so their average size

can not be given in this state. Moreover, it seems that the grain size of the matrix was refined to be about 200  $\mu\text{m}$  with the electric current. Further SEM-EDS was performed to confirm grain-boundary segregation of copper precipitates in the application of electric current. From the EDS mapping of Figure 3, copper-rich precipitates (4 wt.% Fe in Cu) were mainly distributed within the matrix without the electric current (Figure 3a and b) while the precipitates were segregated at the grain boundaries with the electric current (Figure 3c and d).

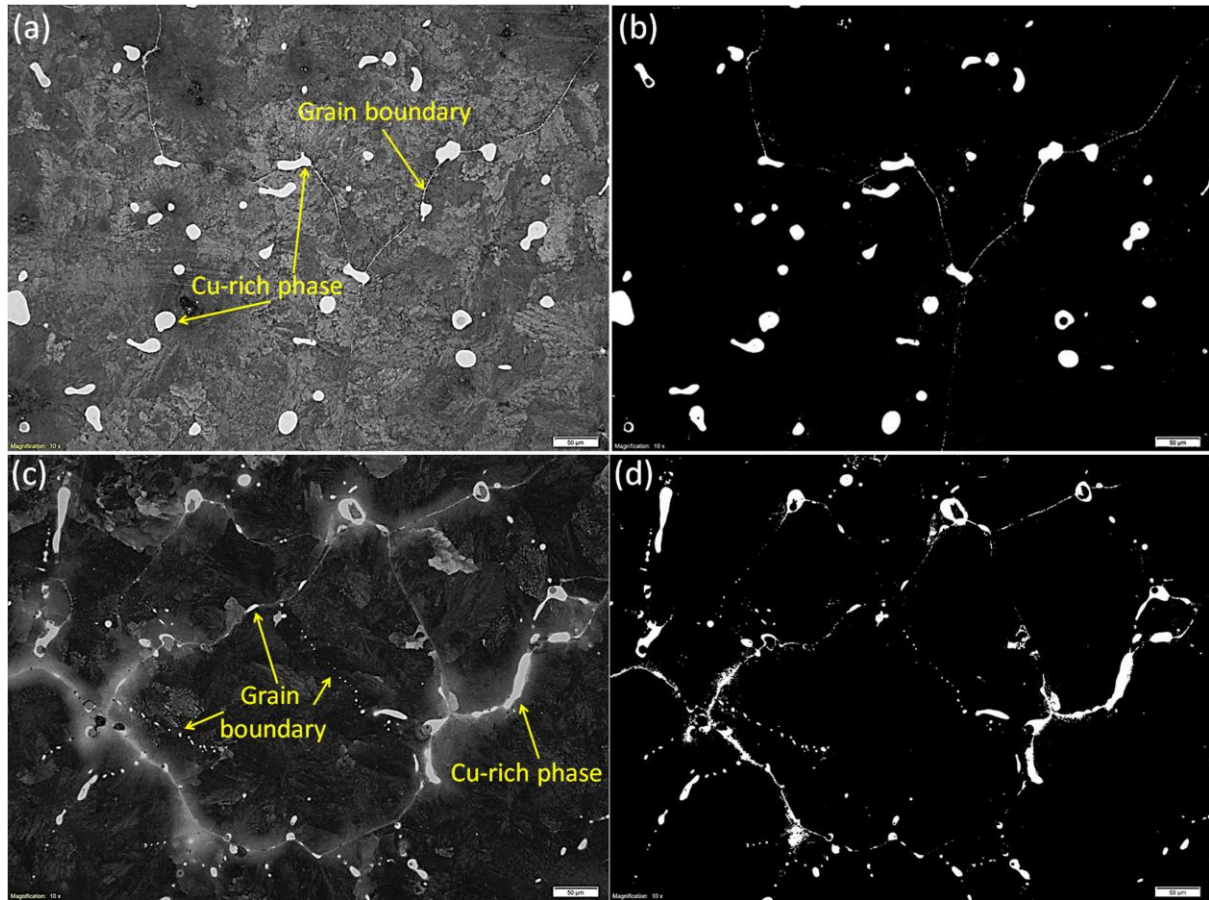


Figure 2. The optical micrographs for the specimens (a,b) before and (c,d) after the pulsed electric current show the distribution of micrometre-sized copper precipitates in the Stage I. Grain-boundary segregation during the solidification can be observed in the pulsed steel, while the copper precipitates dispersion was observed mostly within the ferrite matrix in the untreated steel.

High resolution TEM is implemented to further analyse the distribution of copper precipitates in the nano-size before and after the pulsed electric current (Figure 4). Figure 4a and b show a

TEM bright field image and selected area diffraction pattern for the alloy without the electric current. From the calculations of lattice parameter and crystal structure, the dark spherical particle was determined to be copper. The size of the copper precipitate was ranged from 11.5 nm to 72.4 nm, so the diffraction pattern was presented a polycrystalline diffraction ring. Three distinct distributions of copper precipitates were observed in the Fe-Cu alloy without the electric current, namely, (1) dispersion within the ferrite matrix, (2) dispersion within the cementite, and (3) dispersion at the interphase boundaries between the ferrite and cementite. Through statistical analysis, the copper precipitates dispersion was observed mostly within the ferrite matrix. Moreover, these nano-sized copper precipitates were enriched in a zone (or a cluster), and each zone had approximately 80 particles. When the electric current was applied to the alloy, the distribution of copper precipitates exhibited a significant change (Figure 4c). The dark elongated precipitates were distributed along the interphase boundaries between the ferrite and cementite. There is no precipitate within the matrix of ferrite and cementite. The EDS of Figure 4d can confirm the composition of copper precipitate (4 wt.% Fe in Cu). In order to confirm the copper segregation during solid solution decomposition, the untreated alloys were reheated to 1050°C and were furnace cooled to room temperature with and without electric current. Experimental results show that copper precipitates dominated along interphase boundaries in the pulsed alloy while the precipitates nucleated mostly within ferrite and cementite and minutely at the interphase boundaries in the untreated alloy. These strongly suggest that the copper segregation is greatly promoted by the pulsed electric current.

Previously it had been reported that a copper-rich phase containing 4 wt.% Fe (or less) had been shown to precipitate during the decomposition of austenite in Fe-Cu alloys [10-12]. Normally, the copper content in the investigated Fe-Cu alloy was less than 6 wt.%, so the copper was completely dissolved into the austenite in the thermally-aged Fe-Cu alloys [10-12]. Thus the nano-sized copper phases were observed to precipitate from a supersaturated austenite solid solution during cooling [10-12]. Its distribution also exhibited three distinct distributions as mentioned above. This indicated that nano-sized precipitates were produced during the decomposition of austenite in the present work (e.g. Stage II in Figure 1). The Fe-13.6Cu system containing a large amount of copper that exceeds the solubility limit (6 wt.%) in austenite was investigated currently, so the excess copper unable to dissolve into the austenite would inevitably precipitate in the solidification (e.g. Stage I in Figure 1). In other



words, grain-boundary segregation of copper precipitates in Figures 2 and 3 should occur during the solidification (Stage I) while interphase segregation of copper precipitates in Figure 4 should occur during the decomposition of the supersaturated austenite solid solution.

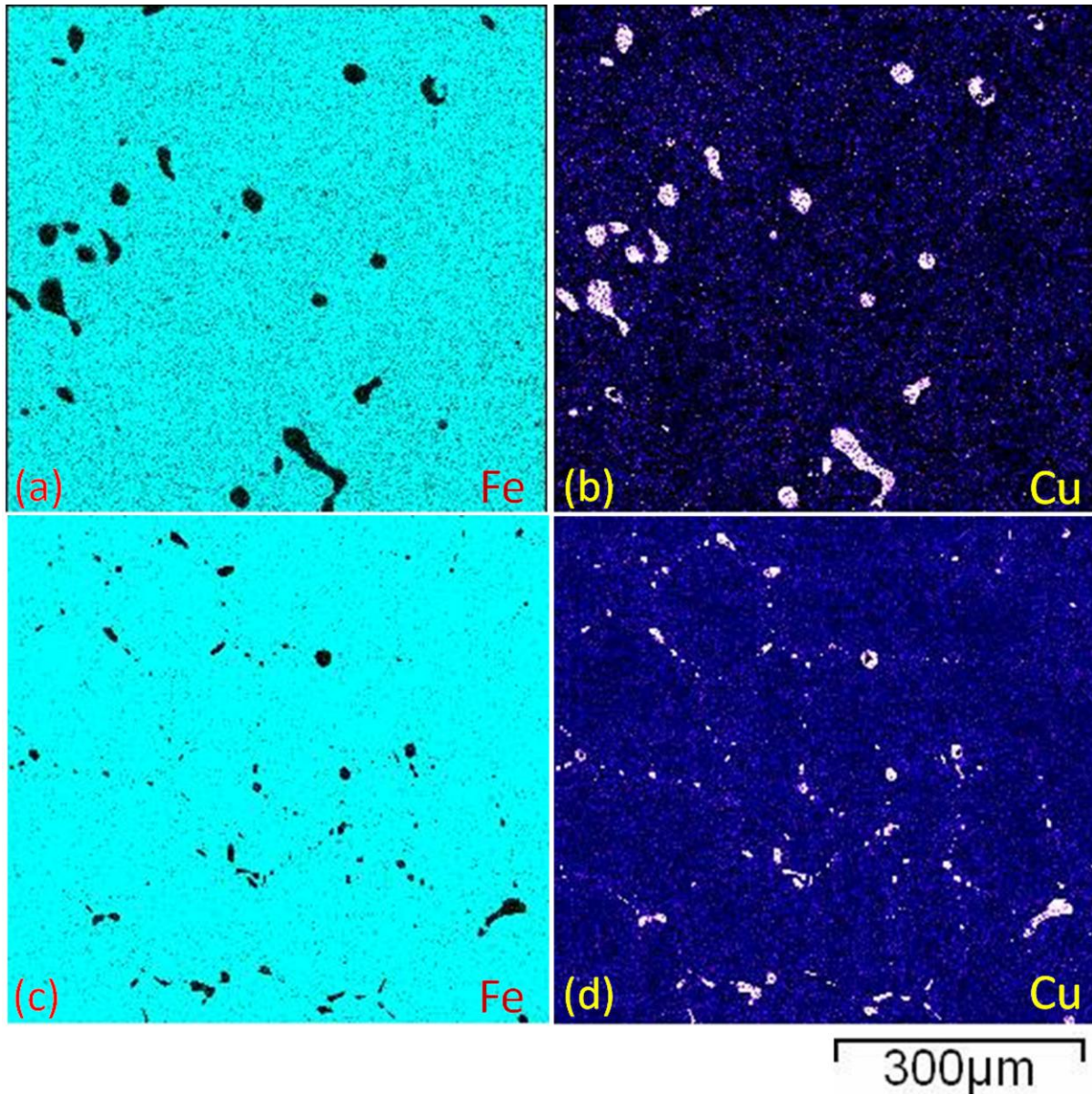


Figure 3. EDS mapping shows the distribution of the Fe and Cu elements (a,b) in the pulsed and (c,d) untreated alloys in the Stage I. Copper-rich precipitates (4 wt.% Fe in Cu) were mainly distributed within the matrix without the electric current while the precipitates were segregated at the grain boundaries with the electric current.



Before discussing the segregation process of copper precipitates in an Fe-Cu alloy under electric current, the mechanism of grain refinement of austenite in pulsed alloy during solidification will be addressed briefly. In the investigation of coarse-grained Cu-Zn alloys, nanophases or ultrafine-grained microstructure can be obtained by applying pulsed electric current [7,15]. It is believed that the nucleation rate of the product is increased by the decrease of thermodynamic barrier during phase transformation. In this study, pulsed electric current was applied to the austenite solidification from the molten alloy (Figure 1). The nucleation rate of the austenite will be also increased by the decrease of thermodynamic barrier during solidification. The newly-formed crystal nuclei will move freely in the molten metal, thereby promote the multiplication of the crystal nuclei and grain refinement.

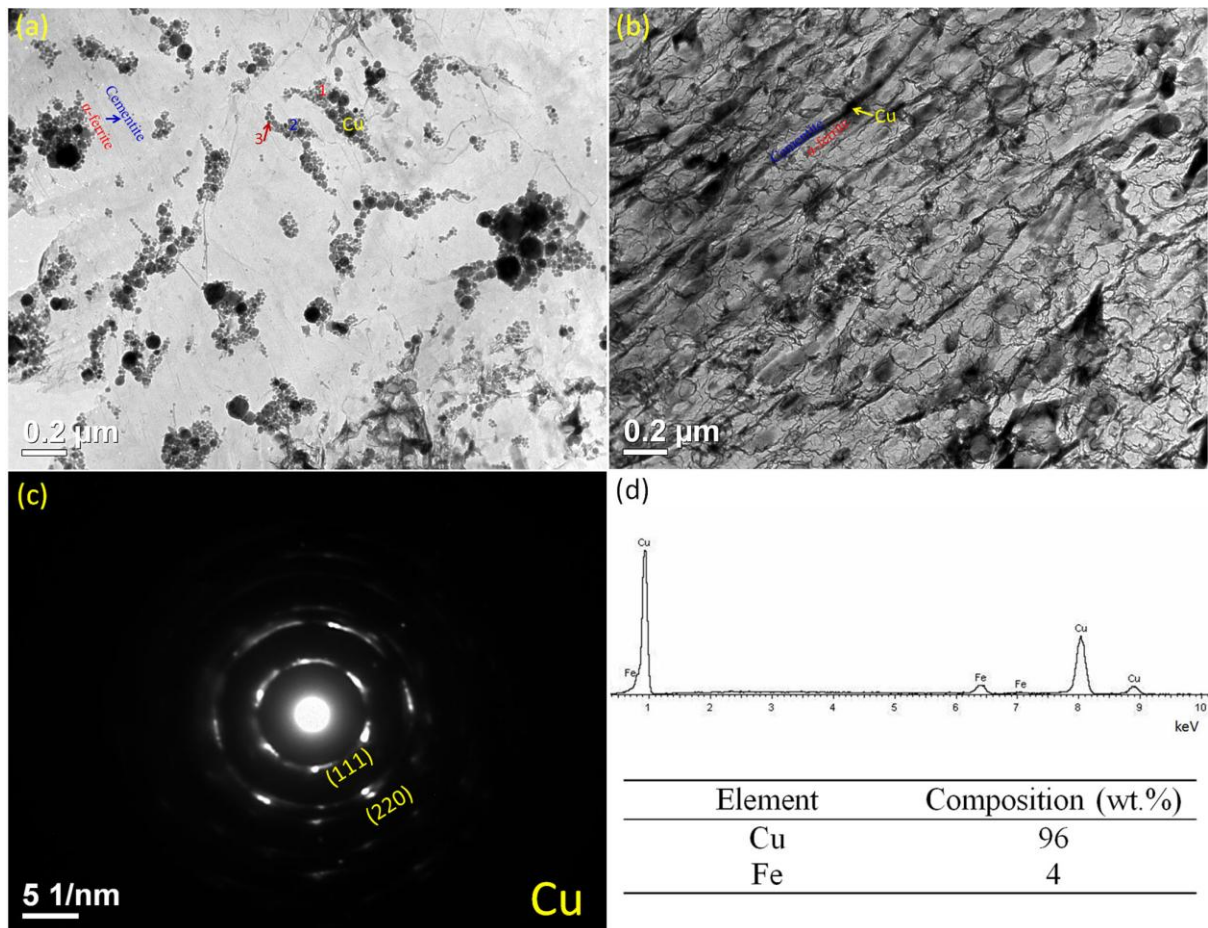


Figure 4. TEM bright field images show the distribution of copper precipitates in the nano-size (a) before and (b) after the pulsed electric current in the Stage II. Three distinct distributions of copper precipitates were observed in the Fe-Cu alloy without the electric current, namely, (1) dispersion within the ferrite matrix, (2) dispersion within the cementite, and (3) dispersion at the interphase boundaries between the ferrite and cementite. The dark

elongated precipitates were distributed along the interphase boundaries between the ferrite and cementite for the pulsed steel. (c) Selected area diffraction pattern for the dark spherical particle presented a polycrystalline diffraction ring. (d) The EDS confirmed the composition of copper precipitate.

Following sections are given to physically explain the grain-boundary segregation and interphase segregation of copper precipitates under pulsed electric current. The thermodynamics of segregation is described by the Langmuir-McLean equation [3]:

$$\frac{\theta_i}{1 - \theta_i} = x_i \exp(-\Delta G_i / RT) \quad (1)$$

where  $\theta_i$  is the occupancy of the grain boundary site or interphase sites with the segregating element  $i$ ,  $x_i$  is the mole fraction of the solute element  $i$  in the bulk, and  $\Delta G_i$  is the free energy of segregation. According to thermodynamics the segregation increases with decreasing free energy and with increasing bulk concentration. In the solidification (Stage I), a large bulk concentration should have increased the segregation in untreated alloy (e.g. thermal diffusion segregation). In the experiment, only 15.4% copper precipitates were segregated at the grain boundaries while majority of copper precipitates ( $\sim 84.6\%$ ) were dispersed in the matrix. It suggested that energy barrier for segregation at grain boundaries should be much higher at this stage, thereby retarded the segregation. Experimental results have confirmed that the copper precipitates prefer to segregate at dislocations and stacking faults within the matrix in the thermal diffusion segregation [1,10,11]. However, the grain-boundary segregation of copper precipitates can be observed in pulsed alloy. It indicated that energy barrier for segregation at grain boundaries must be decreased. When an electric current passes through a conductor, their system free energy encloses an additional term  $G_e$  in comparison with the system without electric current but at the same state (temperature, pressure, and constituents etc.). The homogeneous distribution of electric current is modified by the presence of the precipitates because of their different electrical conductivity with the matrix. This causes the change of electric current associated free energy  $\Delta G_e$ . For simplicity, the general expression of  $\Delta G_e$  can be expressed as follows [9,16]:

$$\Delta G_e = \frac{\sigma_1 - \sigma_2}{2\sigma_1 + \sigma_2} k j^2 V \quad (2)$$

where  $\sigma_1=8.3\times10^5\ \Omega^{-1}\text{m}^{-1}$  and  $\sigma_2=4.76\times10^6\ \Omega^{-1}\text{m}^{-1}$  are electric conductivities of the austenite and copper precipitate at 1100 °C, respectively.  $k$  is a positive geometry factor.  $V$  is the volume of a precipitate.  $j$  is the current density. Thus  $\Delta G_e < 0$  due to  $\sigma_1 < \sigma_2$ , meaning that the free energy of segregation  $\Delta G_i$  should be much negative due to the an additional term  $\Delta G_e$ . According to Eq. (1), the segregation toward grain boundary in pulsed alloy increases with decreasing free energy and with increasing bulk concentration. In the case of interphase segregation (Stage II), the inequality  $\Delta G_e < 0$  is still valid because the electrical conductivity of copper is higher than that of ferrite and cementite. The nano-sized precipitates were therefore pushed toward the interphase boundaries between ferrite and cementite during the decomposition of austenite. For the untreated alloy, the precipitates would nucleate mostly within ferrite and cementite and minutely at the interphase boundaries due to the higher free energy barrier.

The kinetics in the pulsed and untreated alloys was also different. In the application of electric current, the atomic diffusion can be enhanced [5,6]. Possibilities for enhancing the diffusion by pulsed electric current include an increase in the diffusion pre-exponential factor and/or a reduction in the diffusion activation energy [6]. In general, the segregation is closely related to the process of diffusion, e.g., the segregation is exacerbated by the enhanced diffusion in the pulsed alloy. Based on the thermodynamic and kinetic aspects, this kind of electric current-induced segregation was much stronger than the thermal diffusion segregation.

Furthermore, the bulk electrical conductivity of the untreated alloy is measured to be  $4.3\times10^6\ \Omega^{-1}\text{m}^{-1}$ , while that of the pulsed alloy is  $7.1\times10^6\ \Omega^{-1}\text{m}^{-1}$ . The electrical conductivity of the alloys is raised 1.65 times after electric current treatment. It suggests that the microstructure evolution induced by the electric current greatly increases the system electrical conductivity. The possibility of the conductivity improvement by pulsed electric current is due to the reduction in the grain-boundary/interphase-boundary resistance caused by high conductivity copper segregation.

#### **4. Conclusions**

In summary, results of this electric current approach are applied to the Fe-Cu system presenting two stages of segregation, namely, grain-boundary segregation during the solidification and interphase segregation during the decomposition of a solid solution. Segregation occurs as a result of homogeneities in a solid. These homogeneities provide sites on which solute atoms have a lower Gibbs free energy. Such sites occur at grain boundaries and interfaces between different phases. All of these regions have solute concentrations that differ from each other and from that of the bulk material. Based on the thermodynamic and kinetic aspects, the segregation process of copper precipitates in the Fe-13.6Cu alloy under electric current would be of great interest and of physical importance because this kind of electric current-induced segregation was much stronger than the thermal diffusion segregation.

#### **Acknowledgements**

The authors are grateful to Professor Kenneth C. Mills at Imperial College London for fruitful discussions. The work was financially supported by EPSRC (No. EP/J011460/2) and the Royal Academy of Engineering at United Kingdom.

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